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The Hydroisomerization of *n*-Butenes

I. The Reaction of 1-Butene over Alumina- and Silica-Supported Rhodium Catalysts

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The reaction of 1-butene with hydrogen has been studied using alumina- and silica-supported rhodium catalysts in the temperature range −20° to 80°C. The kinetics and apparent activation energies for hydrogenation and isomerization are reported. The initial (cis/trans) ratio in 2-butene is greater than the thermodynamic equilibrium value; this ratio decreases as the temperature is increased. The support appears to have little effect.

Possible mechanisms for hydrogenation and isomerization are discussed. Isomerization is thought to proceed via a 1-methyl-π-allyl intermediate and the implications of this postulate are discussed.

INTRODUCTION

Several studies of the hydrogenation exchange and isomerization of monoolefins using rhodium catalysts have been reported (*1*, *2*, *3*). The results show that, when compared with other Group VIII metal catalysts, rhodium is anomalous in that relative rates of exchange and isomerization exhibit a marked temperature dependence, increasing rapidly as the temperature is increased. This paper reports the results of a further investigation of the hydroisomerization of 1-butene using alumina- and silica-supported catalysts.

EXPERIMENTAL

Catalysts. The 5% Rh/Al_2O_3 catalyst was supplied by Johnson, Matthey & Co., Ltd; 5% Rh/SiO_2 catalyst was prepared by the evaporation of an aqueous solution of $RhCl_3 \cdot 3H_2O$ onto Aerosil (Degussa Ltd.). The supported salt was dried and reduced at 220°C for 18 hr using three successive volumes of hydrogen. Catalyst samples were activated immediately before use by treatment in 150 mm of hydrogen at 220°C for 1 hr.

Apparatus, materials, and methods. 1-Butene, from Matheson Co., Inc., was merely degassed before use. Cylinder hydrogen was freed of trace impurities by diffusion through a palladium-silver alloy thimble.

The catalyst rested on the bottom of a cylindrical Pyrex glass reaction vessel of volume 100 ml. The vessel was connected to a conventional vacuum apparatus which was maintained at 10^{-5} torr or better by means of an oil-diffusion pump backed by an oil rotary pump. The required pressures of reactants were admitted to the reaction vessel from a storage vessel containing the reaction mixture at the required composition. Reactions were followed by the pressure fall observed using a calibrated glass spiral gauge. At the required conversion the reaction products were extracted by expansion into an evacuated vessel whence they were transferred to the analysis system.

Analysis. Analysis of reaction products was carried out by gas chromatography using a 20-ft long column packed with silver nitrate–benzyl cyanide supported on 60-80 mesh Silocel firebrick. The column was operated at ambient temperature with nitrogen as flow gas. The column gave excellent separation of the reaction products, corrected retention volumes for *n*-butane, *trans*-2-butene, 1-butene and *cis*-2-butene being 250, 450, 575, and 700 ml respectively.

RESULTS

Calculation of reaction rates. Initial rates of hydrogenation, r_h, were calculated (*4*) from the plots of pressure fall against time. Rates of isomerization, r_i, were calculated using the expression previously used by Twigg

$$r_i = \{\log_{10}(1 - y_{eq}) - \log_{10}(y - y_{eq})\} [2.303(1 - y_{eq})(P_B)_0/t]$$

where y is the fraction of reactant olefin remaining; y_{eq}, the fraction of reactant olefin at equilibrium; t, the time of reaction; and $(P_B)_0$, the initial pressure of 1-butene.

The course of reaction. The distribution of reaction products as a function of hydrogen uptake was studied over the Rh/Al_2O_3 catalyst in the temperature range —20° to 153°C and over the Rh/SiO_2 catalyst between —16° and 75°C. The results are summarized in Fig. 1, which shows plots of butene distribution against butane yield for three temperatures using each catalyst. In each series the ratio of the pressure of hydrogen to that of 1-butene was unity.

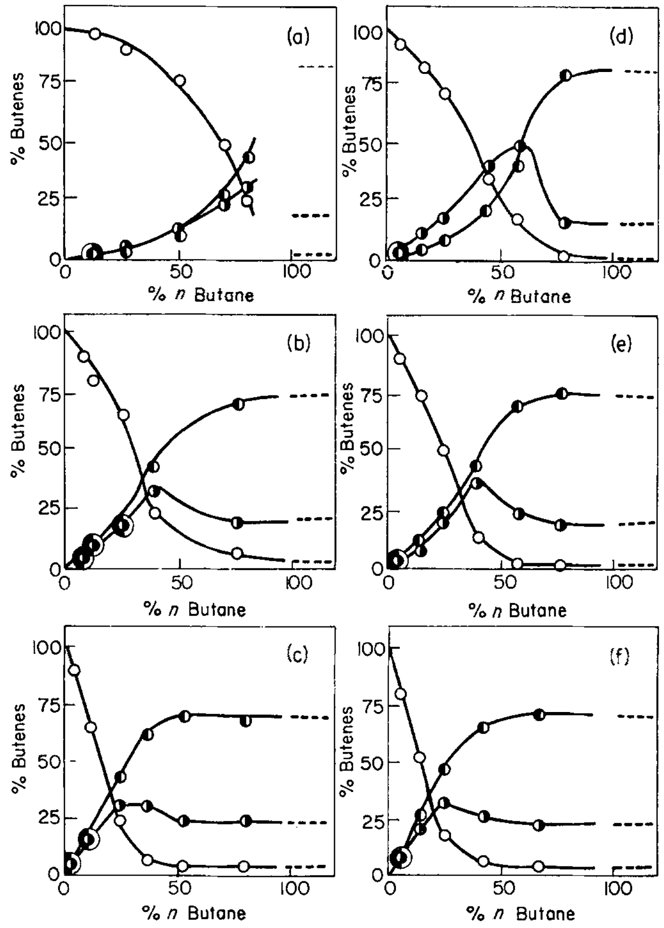


FIG. 1. Variation of butene distribution with hydrogen uptake (expressed as *n*-butane yield) for Rh/Al_2O_3 at (a) —20°C; (b) 25°C, and (c) 67°C; and for Rh/SiO_2 at (d) —16°C; (e) 25°C, and (f) 75°C. Broken lines show thermodynamic equilibrium values; ○, 1-butene; ◐, *trans*-2-butene; ◐, *cis*-2-butene.

TABLE 1
INITIAL RATE ORDERS IN HYDROGEN AND 1-BUTENE FOR HYDROGENATION AND ISOMERIZATION

Catalyst	Temp. (°C)	$(P_B)_0$ (mm)	$(P_{H_2})_0$ (mm)	Hydrogen order		Butene order	
				Hydrogenation	Isomerization	Hydrogenation	Isomerization
Rh/Al_2O_3	0°	30.0 ± 0.5	15.0 – 120.0	1.0	0.2	—	—
	66°	30.0 ± 1.0	14.2 – 124.5	1.0	0.0	—	—
Rh/SiO_2	0°	30.0 ± 0.5	15.5 – 121.6	1.0	0.0	—	—
	54°	30.0 ± 1.0	14.6 – 121.0	1.0	0.0	—	—
Rh/Al_2O_3	66°	10.2 – 149.8	30.0 ± 1.0	—	—	−0.05	−0.4
Rh/SiO_2	54°	19.0 – 149.5	30.0 ± 0.5	—	—	−0.1	−0.4

Kinetics. Initial rate orders with respect to both reactants for hydrogenation and isomerization were determined using each catalyst in the temperature range 0–66°C. The results are summarized in Table 1.

During the kinetic studies it was observed that the catalyst activity varied slightly from reaction to reaction. To minimize this variation it was necessary to carefully standardize conditions between reactions. Slight variations were then corrected by adopting a standard run technique in which the activity was checked by carrying out alternate reactions with a standard mixture comprising 30 mm 1-butene and 30 mm hydrogen.

Activation energies. The activation energies for hydrogenation (E_h) and isomerization (E_i) were determined using Rh/Al_2O_3 in the range —18–105°C and using Rh/SiO_2 between —18° and 86°C. In each series the initial (P_{H_2}/P_B) ratio was unity. Because of the high activity of both catalysts it was only possible to cover a comparatively small temperature range with a given weight of catalyst. It was, therefore, necessary to carry out two series of reactions over each catalyst in order to cover the required temperature range. The results are summarized in Table 2.

Investigation of support materials. From the foregoing results it is clear that there are some significant differences between alumina-supported and silica-supported rhodium catalysts. To investigate possible support effects two series of reactions were carried out.

In the first series the catalytic activities of the alumina and silica support materials were investigated. Fifty milligram samples of alumina and silica were pretreated in *exactly* the same manner as the supported rhodium catalysts. The catalytic activity for 1-butene hydroisomerization was then investigated using a 1:1 reaction mixture at a total pressure of 60 ± 1 mm. With silica no hydrogenation or isomerization was observed in the temperature range 0° to 154°C in 12 hr. With alumina, however, both reactions occurred at temperatures between 21.5° and 101°C. The results are summarized in Table 3. From these results it can be seen that the alumina possesses an appreciable isomerization activity, the butenes attaining their thermodynamic equilibrium proportions at 101°C in 3 hr.

In the second series of experiments the Rh/Al_2O_3 and Rh/SiO_2 catalysts were thoroughly mixed with an equal quantity

TABLE 2
ACTIVATION ENERGIES FOR HYDROGENATION (E_h) AND ISOMERIZATION (E_i)

Catalyst	Temperature range (°C)	E_h (kcal $mole^{-1}$)	E_i (kcal $mole^{-1}$)
Rh/Al_2O_3	−18° to 27.5°	6.0 ± 0.5	10.0 ± 0.5
	56° to 105°	5.0 ± 1.0	9.7 ± 0.5
Rh/SiO_2	−18° to +18°	9.2 ± 1.0	11.0 ± 0.5
	41° to 86°	8.5 ± 1.0	10.0 ± 1.0

TABLE 3
RESULTS OBTAINED WITH ALUMINA AS CATALYST

Temperature (°C)	Time of reaction (min)	% C_4H_{10}	Butene distribution (%)		
			1-B	*trans* 2-B	*cis*-2-B
21.5°	30	trace	99.3	0.3	0.4
52.0°	30	trace	98.1	0.9	1.0
101.0°	30	2.0	39.7	37.6	22.7
101.0°	180	14.6	6.9	65.5	27.6

of alumina and possible synergistic effects were examined. The results showed that the butene distribution was unaffected by the presence of the support. The only effect of the added alumina appeared to be a reduction in the specific rates of isomerization and hydrogenation, the ratio (r_i/r_h) being unaffected.

1-Butene isomerization in the absence of hydrogen. A sample of the Rh/Al_2O_3 catalyst (0.0075 g) was reduced as previously described and the catalyst vessel was then evacuated at 295°C for 6 hr to remove as much surface hydrogen as possible. 1-Butene, 30 mm, was then admitted to the reaction vessel at either 26.5° or 116°C. Analysis of reaction products after 1 hr showed that no hydrogenation occurred although a small amount of isomerization was observed. The latter was, however, almost insignificant when compared with the amount of isomerization in the presence of hydrogen.

DISCUSSION

The results presented above show that overall the general features of the reaction are similar over the two catalysts. Thus, the kinetics for both hydrogenation and isomerization are similar over the two catalysts, as are the activation energies for isomerization and the initial butene distributions, e.g., both catalysts show an initial cis–trans ratio >1.

The initial rate kinetics for hydrogenation are consistent with a mechanism in which the catalyst surface is effectively saturated with olefin, and hydrogen is less strongly adsorbed than 1-butene. The initial rate order of unity in hydrogen for the addition reaction is compatible with either of two mechanisms: First, the interaction of adsorbed C_4H_8, which we postulate as being in the form of a π-complex, with molecular hydrogen, viz.,

Reaction Scheme A

$$C_4H_8(g) + [*] \rightleftharpoons C_4H_8(a) \qquad (a, a')$$

$$C_4H_8(a) + \underset{*}{\overset{H_2}{\vdots}} + [*] \rightleftharpoons C_4H_9(a) + H(a) \qquad (1, 2)$$

$$C_4H_8(a) + H(a) \rightleftharpoons C_4H_9(a) + [*] \qquad (3, 4)$$

$$C_4H_9(a) + H(a) \rightarrow C_4H_{10} + [*] \qquad (5)$$

or second, a Langmuir-Hinshelwood mechanism involving reaction between adsorbed olefin and an adsorbed hydrogen atom, viz.

Reaction Scheme B

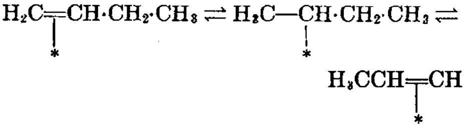
$$C_4H_8(g) + [*] \rightleftharpoons C_4H_8(a) \qquad (a, a')$$

$$H_2(g) + 2[*] \rightleftharpoons 2H(a) \qquad (b, b')$$

$$C_4H_8(a) + H(a) \rightleftharpoons C_4H_9(a) + [*] \qquad (1, 2)$$

$$C_4H_9(a) + H(a) \rightarrow C_4H_{10}(g) \qquad (3)$$

The initial rate order of zero in hydrogen for isomerization suggests that, if alkyl reversal

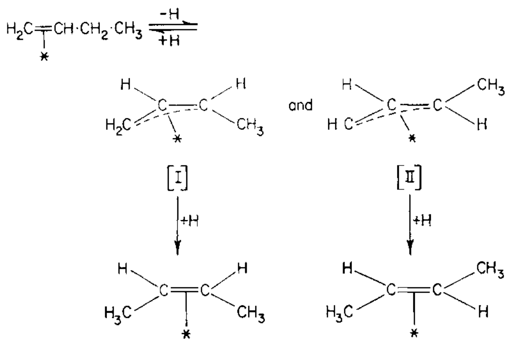


$$\underset{*}{H_2C{=}CH}{\cdot}CH_2{\cdot}CH_3 \rightleftharpoons H_3C{-}\underset{*}{CH}{\cdot}CH_2{\cdot}CH_3 \rightleftharpoons H_3C\underset{*}{CH{=}CH}{\cdot}CH_3$$

is responsible for double-bond migration, olefin desorption [step (a′)] is rate-determining, since in either of the above mechanisms $\theta_{C_4H_9} \propto P_{H_2}^{0.5}$ and any other step would lead to an order of 0.5 or unity. However, if step (a′) was rate-controlling it might be expected that the rate of isomerization would show a zero or positive dependence upon the butene pressure and that $E_i < E_h$. Experimentally an initial rate order of —0.4 and an ($E_i - E_h$) value of >0 are observed.

An alternative route to the formation of 2-butene may be postulated as involving an interconversion between adsorbed olefin and a π-allyl-adsorbed intermediate (*5*, *6*).

Reaction Scheme C



The adsorbed 1-methyl-π-allyl intermediate may exist in two conformations, [I] and [II], which give rise, respectively, to *cis*- and *trans*-2-butene. Assuming that the formation of 1-methyl-π-allyl is the rate-determining step in isomerization, an order of zero in hydrogen would be expected. The negative order in 1-butene can be explained qualitatively by considering that the effect of increasing butene pressure is to decrease the number of surface sites available to accept the ejected hydrogen atom. The higher activation energy for isomerization than for hydrogenation may also be explicable by the above mechanism (*7*).

Several important points emerge from the above postulate. First, the butyl radical produced in the addition reaction must be predominantly 1-butyl rather than 2-butyl, since the latter would give rise to isomerization. Thus one would expect that in the reaction with deuterium 1-butene exchange would be independent of 2-butene formation. Bond *et al.* (*3*) have found that at low temperatures (around 0°C) exchange is more rapid than isomerization using rhodium-alumina catalysts. Second, since the two reactions occur independently, the effect of selective poisons would be to alter the (r_i/r_h) ratio more markedly than if the reactions were concomitant. Evidence that this is the case will be presented in another paper (*8*). Third, isomerization should occur in the absence of hydrogen by inter- or intramolecular hydrogen transfer; and fourth, the 2-butene distribution will depend upon the relative stabilities of the *syn* and *anti* conformations of adsorbed 1-methyl-π-allyl, rather than upon the conformation of adsorbed 2-butyl as suggested elsewhere (*9*). Using the latter approach, and assuming approximately equal interaction energies for Me–Me and Me–surface, a maximum (cis/trans) ratio of unity would be expected. Furthermore the (cis/trans) ratio should increase with increasing temperature rather than decrease, as is experimentally observed.

The butene distributions (Fig. 1) show that the initial (cis/trans) ratio in 2-butene was >1. Furthermore, as the reaction proceeded the yield of *cis*-2-butene exceeded its thermodynamic equilibrium amount, passing through a maximum, the height of which increased as the temperature was decreased. This preferential formation of the thermodynamically less stable cis isomer is not uncommon in rhodium-catalyzed isomerizations, having been observed in $RhCl_3$-catalyzed isomerization of 1-pentene (*10*, *11*) in the $[acacRh(C_2H_4)_2]$-HCl or $[(C_2H_4)_2RhCl]_2$-HCl catalyzed isomerization of 1-butene

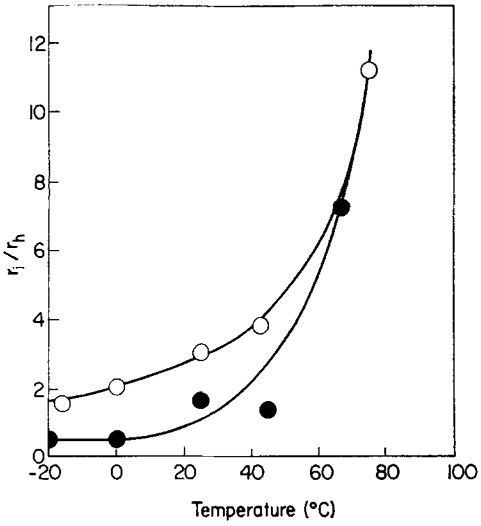


FIG. 2. Variation of the ratio (r_i/r_h) with temperature for Rh/SiO_2 (○) and Rh/Al_2O_3 (●).

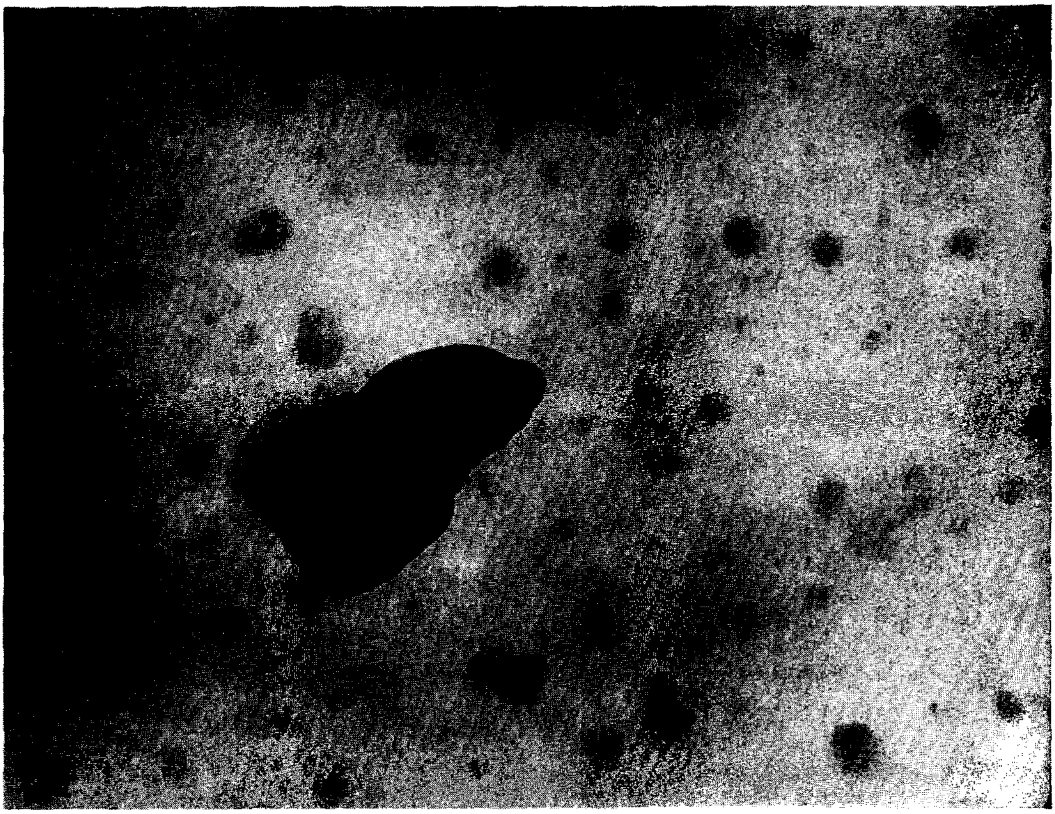


FIG. 3. Electron micrograph of Rh/Al_2O_3 catalyst, magnification 240,000×.

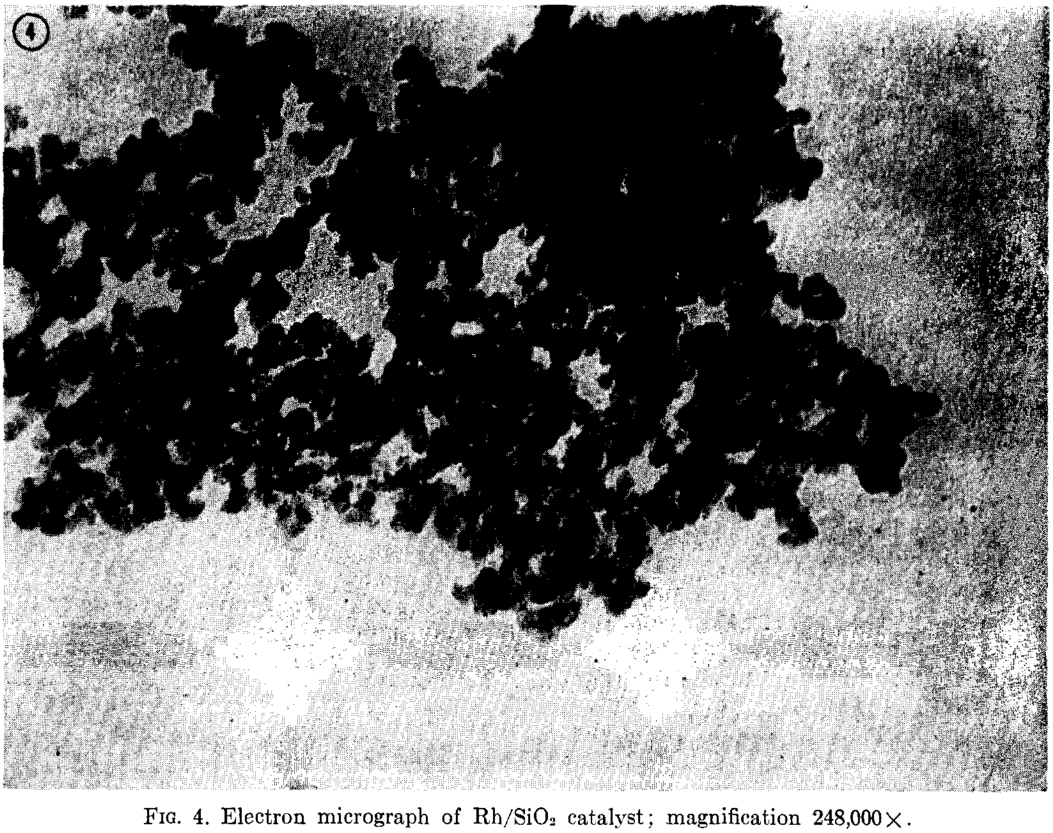


FIG. 4. Electron micrograph of Rh/SiO_2 catalyst; magnification 248,000×.

(*12*) and $RhCl_3$-catalyzed hydrogenation of 1-hexene (*13*).

The form of the *cis*-2-butene yield as a function of hydrogen uptake clearly indicates that the reaction was not diffusion-controlled and, therefore, that the gas-phase concentrations of 2-butenes are a true reflection of their surface concentrations. If we assume that the relative strengths of adsorption decrease in the order

$$\text{1-butene} > \text{cis-2-butene} > \text{trans-2-butene},$$

for which there is considerable indirect evidence (*14*, *15*), we can deduce that at low temperatures the ratio of (syn/anti) conformations of 1-methyl-π-allyl must be >1 and that this ratio decreases as the temperature increases. This is consistent with the observation (*16*) that in the complex $(\pi\text{-}C_4H_7)Co(CO)_3$ increasing temperature favors the anti conformation of 1-methyl-π-allyl.

Our results for the effect of temperature on the butene distribution are in broad agreement with those observed by Bond and co-workers (*2*). Thus at low temperatures rhodium is an apparently "poor" isomerization catalyst whereas at high temperatures it is a "good" isomerization catalyst. These effects can be ascribed to the different temperature dependencies of the rates of competing reactions. Consideration of the plots of the ratio of initial rates of isomerization and hydrogenation (r_i/r_h) against temperature (Fig. 2) shows that the effect is greater with Rh/Al_2O_3 than with Rh/SiO_2. This is as expected since $(E_i - E_h)$ $\sim$5 kcal mole^{-1} with Rh/Al_2O_3 and 1.5 kcal mole^{-1} with Rh/SiO_2.

So far in this discussion we have assumed that the mechanism is essentially the same over the Rh/Al_2O_3 and Rh/SiO_2 catalysts. The results show that under the conditions we have used, the only significant, and perhaps surprising, effect of changing the support was to change the activation energy for hydrogenation. Electron microscopic examination of the two catalysts shows that the distribution and particle size of rhodium is different (see Figs. 3 and 4). These micrographs were obtained by supporting the finely divided catalyst particles on copper grids covered by a carbon film. In the plates the darker areas are the catalyst particles and the electron-opaque black areas are the rhodium metal. From our preliminary investigations we tentatively suggest that the change in E_h is due to the influence of the support upon crystallographic structure of the rhodium, so that different crystal planes are exposed on Rh/Al_2O_3 from those on Rh/SiO_2. Further investigations of the effects of the support are being carried out.

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